



# Removal of Cr(VI) onto functionalized pyridine copolymer with amide groups

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## ABSTRACT

New pyridine strong base anion exchange resin has been prepared by the nucleophilic substitution reaction of 4-vinylpyridine:divinylbenzene copolymer of gel structure with 2-chloroacetamide as halogenated compound. The resulting resin was used to remove Cr(VI) from the aqueous solution. Batch adsorption studies have been carried out to determine the effect of the initial concentration of Cr(VI), adsorbent dose, pH, temperature and the presence of sulfate anions as counter ions. The process was found to be pH, solid/liquid ratio and concentration dependent. The adsorption capacities increase with the increase of the initial concentration of Cr(VI) and therefore, the resin exhibited the degree of usage of the strong base exchange capacities higher than 90% and the good efficiency in the chromium removal. At acidic pH and low concentration of the hexavalent chromium the synthesized pyridine resin offer much greater chromate removal capacities compared to alkaline pH. Equilibrium modeling of the process of Cr(VI) removal was carried out by using the Langmuir and Freundlich isotherms. The experimental data obeyed these isotherm models. Thermodynamic studies were performed and the parameters namely,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  showed the spontaneous and endothermic process of the adsorption of Cr(VI) on the pyridine resin. In the competitive adsorption studies, chromate/sulfate revealed the selectivity of the pyridine adsorbents towards chromium ions. This selectivity is explained by the adsorption of the transition metal anion on the  $\pi$  bonds of the pyridine ring and the formation a sandwich arrangement with chromium anion and amide functional groups attached to the quaternary nitrogen atoms.

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## 1. Introduction

The discharge of toxic and polluting metal ions into the environment and municipal sewers by the mining, metallurgical, electroplating, electronic, nuclear and other industries constitutes one of the major causes of ground water contamination. One of the major toxic metal ions endangering human life is Cr(VI) which is produced because of the extensive use of chromate and dichromate in metal plating, pigment manufacturing, leather tanning, stainless production and as corrosion control agents in the cooling waters.

Cr(VI) is an anion that mainly exists as oxy-anion in the aqueous phase in the form of  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$ , dependent on the pH and total concentration of the solution. Cr(VI) in acidic solution demonstrates a very high positive redox potential which denotes that it is strongly oxidizing and unstable in the presence of electron donors. Above pH 7, only  $\text{CrO}_4^{2-}$  ions exist in the solution throughout the concentration range; in the pH 1 and 6,  $\text{HCrO}_4^-$  is predominant. It is well-known that Cr(VI) is toxic to living system and its prolong exposure may cause cancer in the digestive tract and lungs [1]. Thus, the removal of this metal ion from dilute wastew-

aters has become an important and widely studied area where a number of technologies have been developed over the years such as, precipitation, co-precipitation and filtration.

In the recent years attention was focused on the methods for recovery and reuse of metals rather than disposal. These include activated carbon adsorption [3], liquid–liquid extraction [4], liquid membrane separation [5], ion exchange, biosorption [6], chelating resin and reactive polymer methods [7,8].

Removal of Cr(VI) from cooling water and ground water by ion exchanger has been investigated by many researchers and their results have been published [9–22]. The main advantages of the ion exchange are recovery of the metal, selectivity, less sludge volume produced and the meeting of strict discharge specification. Also, it has been a strong alternative to other processes because of its ability to reduce dissolved chromate concentration to no detectable levels in the water treatment plants.

The most important properties of the ion exchange resins that influence their application are resin capacity and rate behavior in addition to sorption selectivity which is basically an attribute of the functional groups of the resin. Although the equilibrium sorption capacity of a resin is dependent on the concentration of functional groups, there is a difference between the equilibrium sorption capacity observed in practice and theoretical capacity, the last being higher. This case is often observed for the resins synthe-

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sized from the functional groups bearing monomers as opposed to those produced by postfunctionalization of the polymeric supports.

Pyridine ion exchangers could represent an alternative for the selective retention of chromate ions. Previous work focused on the thermodynamic and kinetic studies of Cr(VI) retention from the aqueous solutions on the pyridine resins with different lengths of alkyl substituents namely, methyl, ethyl and butyl functional groups at the quaternary nitrogen atom [20–22]. Chromium retention capacity depends on the ionic form of the strong base anion exchangers and the substituent type at the quaternary ammonium atoms. The behavior of the pyridine resin in sulfate ionic form for the sulfate/chromate exchange is untypical compared to the well-established selectivity order for the common anions in the case of styrene commercial strong base anion exchange resins. The pyridine resins exhibited the following order of the selectivity,  $\text{CrO}_4^{2-} > \text{SO}_4^{2-}$ . Selectivity of these strong base anion exchangers was influenced by the concentration of chromium, the ionic form of the resin and the substituent of the alkyl length at the quaternary ammonium atoms.

In the present paper new pyridine strong base anion exchange resin with amide functional groups attached to the quaternary nitrogen atoms has been synthesized. This novel resin was performed by nucleophilic substitution reaction of 4-vinylpyridine: divinylbenzene (4-VP:DVB) copolymer with 2-chloroacetamide. Its adsorption property towards Cr(VI) was studied for different conditions. The investigated parameters that influence adsorption were the initial Cr(VI) concentration, agitation time, pH, resin amount, temperature and the presence of sulfate anions. Equilibrium and thermodynamic studies have also been carried out.

## 2. Experimental

### 2.1. Materials

4-Vinylpyridine (4-VP, supplied from Fluka) was purified by vacuum distillation immediately before to use. Divinylbenzene (DVB, supplied from Fluka), technically pure (80%) contains residual mainly 3- and 4-ethyl vinylbenzene.

The starting 4-VP:8%DVB copolymers of gel morphological type was synthesized by aqueous suspension copolymerization of 4-VP with DVB using 1.5 wt.% of benzoyl peroxide as initiator. The aqueous phase consisted of 3 wt.% NaCl, 0.12 wt.% gelatine and 0.5 wt.% ammonium salt of poly(styrene-co-maleic anhydride). The organic:aqueous phase ratio was 1:3 (v/v).

The copolymerization reaction was allowed to proceed for 10 h at 80 °C and 2 h at 90 °C. After copolymerization, the copolymer beads were separated and extracted with methanol, in a Soxhlet apparatus, to remove traces of residual monomers, linear oligomers of 4-VP. The samples of dried copolymer in the range diameter of 0.4–0.8 mm were characterized by the nitrogen content as determined by elemental analysis. The experimental nitrogen content is 10% compared to the theoretical one (11%) which means that the most part of 4-VP amount reacted with DVB.

The pyridine strong base anion exchange resin was obtained by the nucleophilic substitution reactions of 4-VP:8%DVB copolymer, gel type, with 2-chloroacetamide (ClAc). The quaternization reaction was performed in dimethylformamide in the glass round bottomed flask equipped with a stirrer, reflux condenser and thermometer. The amount of ClAc corresponded to nitrogen: halogenated compounds molar ratio of 1:1.5. The reaction was carried out at 60 °C for 48 h. After this, the beads were isolated by filtration and washed with methanol and finally with distilled water.

Sample of anion exchange resin was regenerated with 5% NaCl solution, followed by washing with distilled water until complete removal of chlorine ions. The yielded compound was character-

ized by the strong base exchange capacity determined by the ion exchange of  $\text{Cl}^-$  for  $\text{SO}_4^{2-}$ . The volumetric strong base anion exchange capacity was determined by the elution of  $\text{Cl}^-$  anions with 5%  $\text{Na}_2\text{SO}_4$  aqueous solution, the chlorine ions being potentiometrically determined with 0.02 N  $\text{AgNO}_3$  aqueous solutions. To calculate the gravimetric strong base anion exchange capacity, the resin was dried at 110 °C to constant weight. The resin beads were sieved at a particle size of 0.4–0.8 mm. After air-drying, the resin was stored for the sorption studies.

A chromium(VI) stock solution of 1000 ppm concentration was obtained from Fisher Scientific Co. and used as a reference standard solution. The standard solution was diluted to the desired concentration using distilled water when needed.

$\text{Na}_2\text{SO}_4$  anhydrous and  $\text{AgNO}_3$  were analytical reagent grades from Merck.

### 2.2. Instrumentation

Atomic absorption spectrometry (Analyst 200, PerkinElmer) was used for the chromium analysis. pH was measured by using a glass electrode SevenEasy Mettler Toledo model pH meter. A shaker with thermostat Grant Instrument of OLS 200 model was used for the adsorption experiments and temperature studies.

Scanning electron microscopy (SEM) studies of the pyridine anion exchangers beads coated with gold were performed using a JEOL Model JMS 6310 microscope. For the cross-section of the beads 3500 magnification was used.

### 2.3. Experimental methods

After air-drying, the resin was stored for the adsorption experimental studies by batch method. Prior to any experiments the resin was carefully treated for changing the ion exchanger to chloride form. The effect of the chromium concentration on the retention capacity was investigated by using Cr(VI) solutions range concentration of 5–1000  $\text{mg L}^{-1}$ . For the exchange equilibrium, a series of swollen resin (0.1 g in the dry state) originally completely loaded with  $\text{Cl}^-$  ions was equilibrated with a 25 mL  $\text{K}_2\text{CrO}_4$  solution of different concentrations at 30 °C in a thermostatic shaker bath for 24 h. The effect of the pH on the removal of chromium ions was investigated for the equilibration of 0.1 g resin with 25 mL of initial chromium for the following concentrations 59; 138 and 270  $\text{mg L}^{-1}$  when the solution pH values were changed using HCl 0.1 M solution. The effect of the resin amount for the adsorption studies was studied in the batch vessel by varying the resin from 0.1 to 1.0 g which were contacted by the 25 mL solution of potassium chromate of 13; 22 and 59  $\text{mg L}^{-1}$  concentrations without the change of the solutions pH for 24 h at  $25 \pm 1$  °C. The kinetic adsorption experiments were conducted at the initial chromium concentrations of 13; 22; 59 and 116  $\text{mg L}^{-1}$  and the ionic conditions were maintained using  $1 \times 10^{-2}$  M  $\text{NaClO}_4$  solution. The solution pH value was not modified during the experiments in order to maintain the same ionic condition in the adsorption process.

The effect of the temperature on the adsorption capacity was studied at different temperatures ranging from 20 to 60 °C for the chromium concentrations of 13; 22; 59 and 116  $\text{mg L}^{-1}$ .

The adsorption of Cr(VI) in the competitive conditions was carried out at initial chromium concentration of 22; 59 and 138  $\text{mg L}^{-1}$  and 1 wt.%  $\text{Na}_2\text{SO}_4$ . The adsorption experiments were performed by contacting 0.1 g resin and 25 mL of chromium solution containing  $\text{SO}_4^{2-}$  ions.

In all experiments studies the resin was separated by filtration and the filtrate was analyzed by AAS spectrometry for Cr(VI) content. The concentration of chromium ions was calculated from the change in metal concentration in the aqueous solution before and

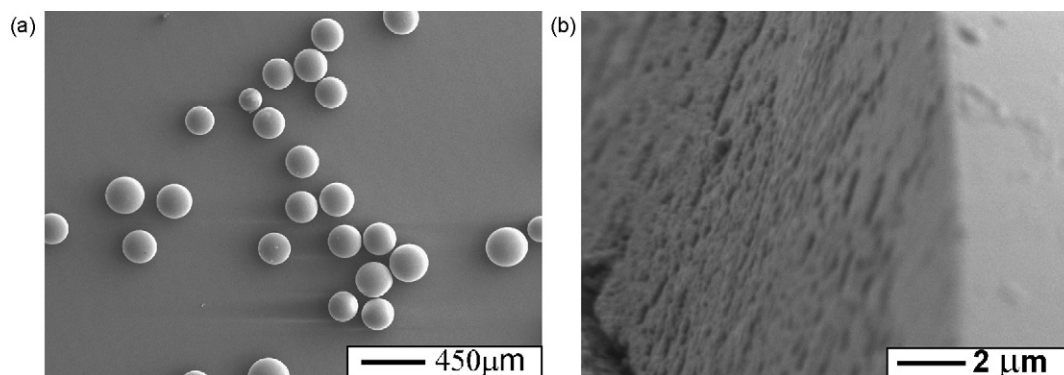


Fig. 1. SEM images of PyR resin: (a) overall view of the resin beads; (b) cross-section of the bead.

**Table 1**  
Characteristics of the performed resin.

Sample code	Structural unit	Strong base anion exchange capacity	
		meq g <sup>-1</sup>	meq mL <sup>-1</sup>
PyR		2.70	1.30

after equilibration adsorption from the weight of the dry resin used using the equation:

$Q(\text{mg/g}) = \frac{(C_i - C_f)V}{m}$ , where,  $Q$  is adsorbed amount,  $C_i$  and  $C_f$  are initial and final concentrations of  $\text{K}_2\text{CrO}_4$  solutions ( $\text{mg mL}^{-1}$ ),  $V$  being the volume of adsorbate solution and  $m$  the dry weight of the beads, i.e. resins.

### 3. Results and discussion

#### 3.1. Synthesis of the pyridine resins

By nucleophilic substitution reactions of 4-VP:DVB copolymers with 2-chloroacetamide as halogenated reactive compound strong base anion exchange resin with amide groups attached to the quaternary nitrogen atoms has been synthesized (Table 1).

The ion exchange capacity is the most characteristic for the ion exchanger and it represents the number of the fixed ionogenic groups  $\text{meq g}^{-1}$  of dry resin in  $\text{Cl}^-$  form for the anion exchangers.

From this table it can be seen that the synthesized strong base anion exchanger has good values of the strong base exchange capacities.

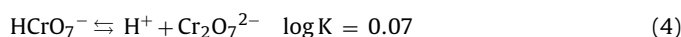
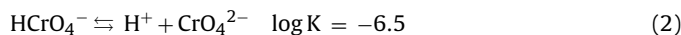
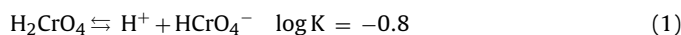
The scanning electron micrographs (Fig. 1) showed the bead shape and gel morphological structures of the prepared PyR sample by the cross-section of the beads.

#### 3.2. Adsorption study

##### 3.2.1. Effect of the initial chromium concentration in the aqueous solution

Effect of chromium ions present initially in the aqueous solution was studied in order to assess the concentration range of chromium which can be treated by this resin. The effect of the initial concentration of chromium hexavalent on the retention capacity and the degree of usage of the strong base anion exchange capacity for the chromate ion sorption without pH changed are presented in Fig. 2.

In this process the anion is not a simple monovalent anion but rather a series of chromate anions depending on the pH and concentration of the solution. The chromate may be present in various forms such as,  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_7^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  in the aqueous solution as a function of pH and concentration and the following equilibria exist between them [14]:



Reaction (3) does not contain any pH term and in the pH range 2–5 this reaction is independent of pH and depends only on the

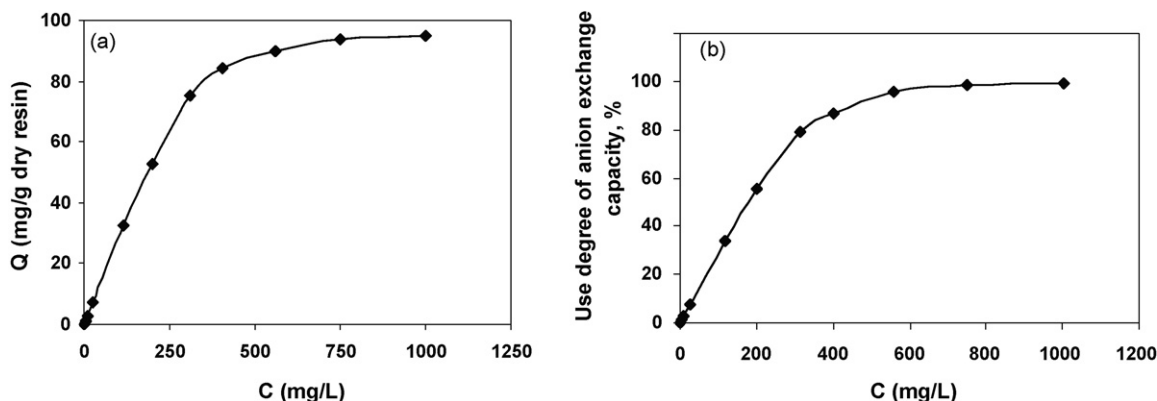
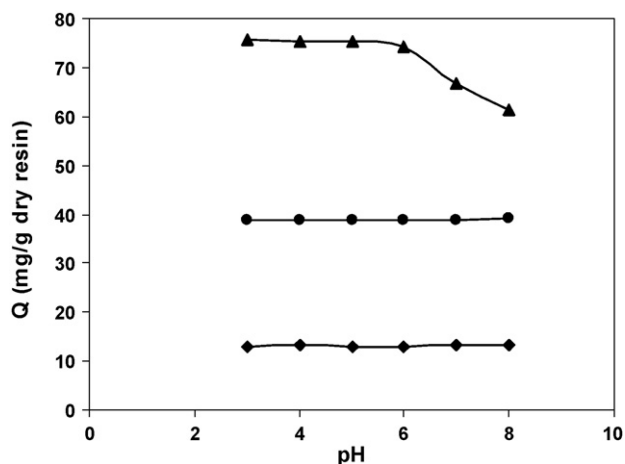
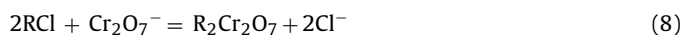
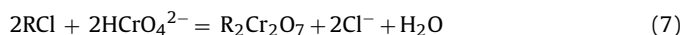


Fig. 2. (a) Effect of  $\text{Cr(VI)}$  concentration on the retention capacity; (b) degree of usage of the strong base anion exchange capacity for PyR resin (0.1 g resin, volume of the adsorption medium, 25 mL; stirring time, 140 rpm; adsorption time, 24 h).



**Fig. 3.** Effect of pH on the adsorption Cr(VI) for pyridine resin at different concentration of the chromate solutions (◆ 59 mg L<sup>-1</sup>; ● 138 mg L<sup>-1</sup>; ▲ 270 mg L<sup>-1</sup>); (resin amount, 0.1 g; volume of the adsorption medium, 25 mL; stirring time, 140 rpm; adsorption time, 24 h).

total Cr(VI) concentration. HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> are the predominant species in the present total chromate concentration range. An anion exchange resin will adsorb chromates from aqueous solution according to the reactions shown in Eqs. (5–8).



The explanation for this finding lies in the influence of the functional groups attached to the quaternary nitrogen atom of the resin, which has a significant effect on the uptake of Cr(VI). There is one principal mean by which the anion exchanger and ions can interact with each other in aqueous solutions which involves the ion exchange of metal ions. This interaction is characterized by the resin structure in terms of the functional groups present.

### 3.2.2. Effect of pH

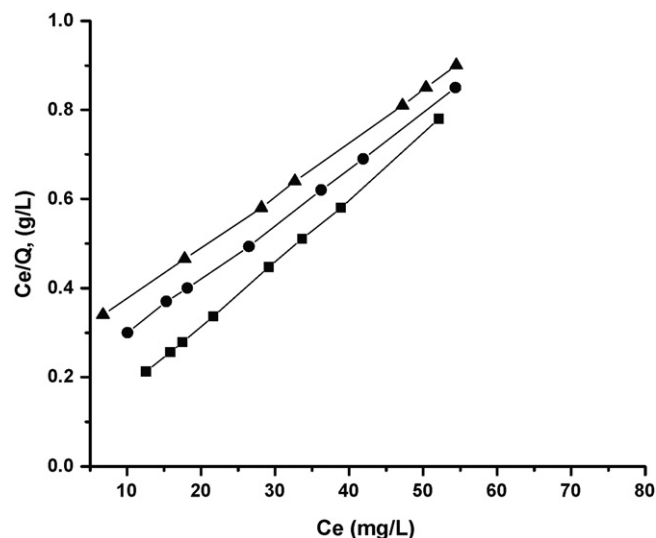
Ion exchange of Cr(VI) was studied at varying pH values to determine the optimum pH range for its removal and the results are presented in Fig. 3. The pH was adjusted with small additions of diluted HCl in the experiments.

The maximum Cr(VI) removal is mainly by an ion exchange mechanism due to the presence of ≡N<sup>+</sup>-CH<sub>2</sub>-CONH<sub>2</sub>, Cl<sup>-</sup> functionality in pyridine resin. Though Cr(VI) exists in several stable forms in aqueous solutions, the relative abundance of any particular species is dependent on pH and Cr(VI) concentration. CrO<sub>4</sub><sup>2-</sup> is predominant in basic solutions, while HCrO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are predominant at pH 2.0–6.0.

As seen in Fig. 3 at low concentration of chromium in the solution the adsorption capacity did not depend on the pH, the resin removed Cr(VI) at the same value in the studied range of pH.

At the high concentration, the behavior of the resin is different, the adsorption capacity decreases when the pH increases. This behavior could be explained by the presence of both HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> species, the chromate anions being in higher amount at pH 8. These divalent ions have a high diameter of the hydrated form that do not allow easy access into the ionic sites of resin and therefore, the retention capacity value has been decreased.

The sorption of Cr(VI) on the resin is clearly very favorable at pH values between 3.0 and 5.0 for the low concentration values of the solution. Cr(VI) is very soluble in aqueous solutions and solubility



**Fig. 4.** Langmuir isotherms for Cr(VI) removal by pyridine resin at different temperatures (▲ 20 °C; ● 30 °C; ■ 40 °C).

increases with pH; therefore, it was practical to employ resins at solution pH values of 8 and below.

### 3.2.3. Adsorption isotherms

For the equilibrium adsorption isotherm in a two-component system consisting of adsorbent and solution a plot of the solute concentration in the solid phase  $Q$  (mg g<sup>-1</sup>) as function of the solute concentration in the solution  $C_e$  (mg L<sup>-1</sup>) at equilibrium gives an adsorption isotherm. In a solid–liquid system, the adsorption results in the removal of solute from the solution onto solid surface until the remaining solute in the solution is in dynamic equilibrium with solute on the solid phase. At equilibrium there is a finite distribution of the solute between the liquid and solid phases, which can be described by many isotherms and adsorption models can be used to fit the observed experimental data and determine the model parameters.

The Langmuir equation was basically derived for the sorption of gases on the solid surface. Nevertheless, it has been extended to include the sorption of solute at solid–liquid interface. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites and the standard mathematical representation is

$$\frac{C_e}{q_e} = \frac{1}{Q^0 \times b} + \frac{C_e}{Q^0} \quad (9)$$

where  $C_e$  is the equilibrium concentration of chromium in the solution (mg L<sup>-1</sup>);  $q_e$ , the amount of the retained chromium (mg L<sup>-1</sup>);  $Q^0$  is the maximum adsorption capacity (mg g<sup>-1</sup>) and  $b$  is the Langmuir constant related to the affinity of the binding sites.

The values of  $Q^0$  were calculated from the slope and intercept of the straight-line plots of  $C_e/q_e$  versus  $C_e$  with a correlation coefficient more than 0.99 (Fig. 4).

The essential feature of Langmuir adsorption can be expressed by means of  $R_L$ , a dimensionless constant referred to as a separation factor or equilibrium parameter for the prediction if the adsorption system is favorable or not.  $R_L$  can be calculated using the Eq. (10):

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

where,  $C_0$  is the initial concentration of the chromate solution (mg L<sup>-1</sup>).

The Freundlich isotherm model assumes that the adsorption of metal ions occurs on a heterogeneous adsorbent surface. Freundlich



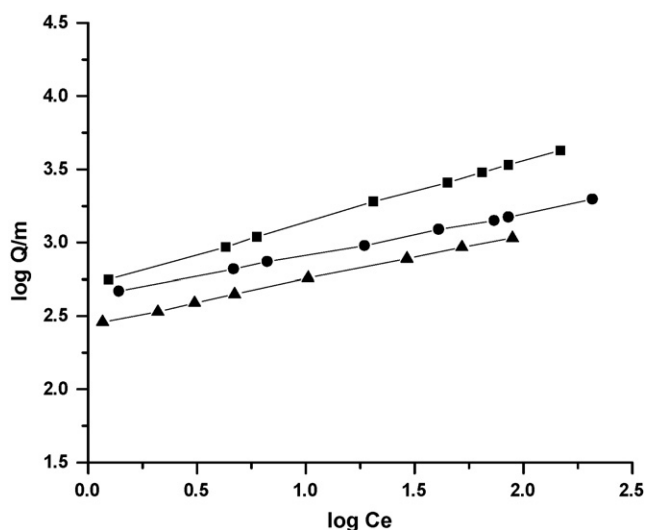


Fig. 5. Freundlich isotherms for Cr(VI) removal by pyridine resin at different temperatures ( $\blacktriangle$  20 °C;  $\bullet$  30 °C;  $\blacksquare$  40 °C).

equation is expressed as Eq. (11):

$$\log \left( \frac{Q}{m} \right) = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

where  $Q$  is the amount of the retained chromium ( $\text{mg L}^{-1}$ );  $m$  is the amount of the resin ( $\text{g L}^{-1}$ );  $C_e$  is the concentration at equilibrium ( $\text{mg L}^{-1}$ );  $K_F$  and  $n$  are Freundlich constants determined by slopes and intercepts of the straight-line of  $\log Q/m$  versus  $\log C_e$  (Fig. 5).

The Langmuir and Freundlich isotherms' parameter values are presented in Table 2.

The parameters clearly suggest for a favorable adsorption of chromate ions. The  $R_L$  values obtained in the present case are less than 1 and very close to 0 and therefore, they also indicates a favorable adsorption [23].

It is clear that experimental data obeyed both Langmuir and Freundlich isotherm models.

### 3.3. Adsorption kinetics

It is a well-established fact that the adsorption of ions in aqueous system follows reversible first-order kinetics when a single species is considered on a heterogeneous surface. There are two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation which are the kinetics and the equilibrium. Kinetics of sorption describing the solute uptake rate which in turn governs the residence time of sorption reaction is one of the important characteristics defining the efficiency of sorption.

The progress of the adsorption process monitored at different time intervals is shown in Fig. 6.

This figure reveals that the adsorbed amount of Cr(VI) constantly increases with increasing time and then levels off after 2 h. In each case, the decreasing concentration of chromium ions remaining in the solution indicates that chromium was adsorbed strongly by all the pyridine resins. The Cr(VI) adsorption with respect to time

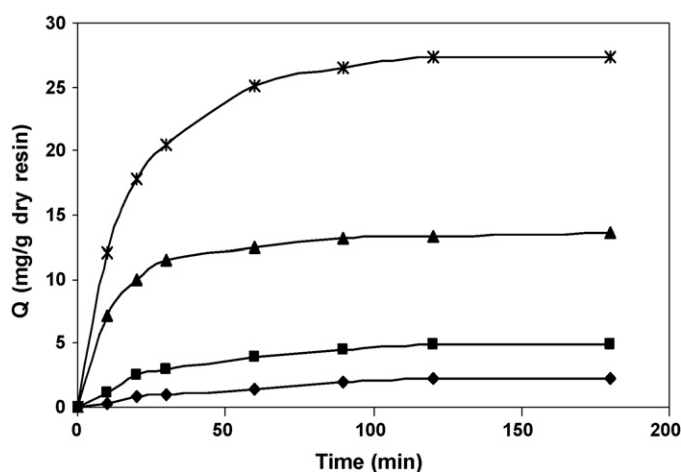


Fig. 6. Effect of the contact time on the sorption of Cr(VI) by PyR (adsorption conditions: initial concentration of Cr(VI)  $\blacklozenge$  13  $\text{mg L}^{-1}$ ;  $\blacksquare$  22  $\text{mg L}^{-1}$ ;  $\blacktriangle$  59  $\text{mg L}^{-1}$ ;  $*$  116  $\text{mg L}^{-1}$  (amount of resin, 0.1 g; volume of the solution, 25 mL; temperature  $25 \pm 1$  °C; stirring time, 140 rpm).

curves is smooth and continuous leading to saturation showing monolayer coverage of metal ion on the surface of the resins.

It is also to be seen that the chromium concentration in these experiments had a pronounced effect on the rate of adsorption; when chromium concentration increased the adsorption rate also increased. Such a concentration effect has also been reported by Chanda and Rempel for the sorption of uranyl sulfate on a reactive polymer-coated gel [16]. Such a concentration effect is not consistent with predictions from the ordinary particle diffusion control model but it is in accord with the shell-core or reacted-layer diffusion control model. The  $t_{1/2}$  (the time needed for 50% of the chromium to be removed) value calculated for low concentrations from the data presented in Fig. 5 was 20 min while  $t_{1/2}$  values for 59 and 116  $\text{mg L}^{-1}$  concentration was 11 min. The  $t_{1/2}$  value decreased as the concentration of hexavalent chromium ions increased. When the chromium concentration increased, the collision numbers between the sorption site and the chromium species increase; this increased the adsorption rate. As a result, the time needed to reach the equilibrium was shortened.

Since the resin beads are constantly agitated during the adsorption process, it is reasonable to assume that the rate is not limited by the mass transfer from the bulk liquid to the beads external surface. One might then postulate that the rate-limiting step may either film or interparticle diffusion.

### 3.4. Adsorbent dose effect

To evaluate the efficiency of pyridine resin on the removal of Cr(VI), adsorption experiments were conducted with different doses of the adsorbent in the range of 0.1–1 g (Fig. 7).

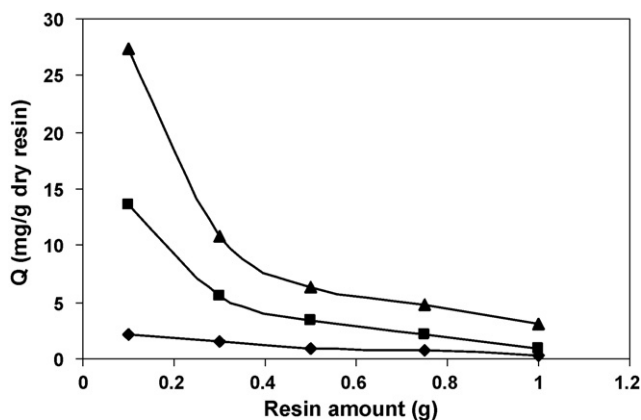
From these figures it is apparent that by increasing the resin amount, the adsorption efficiency increases but the adsorption density, the amount adsorbed per unit mass, decreases. It is readily understood that the number of available adsorption sites increases by increasing the resin amount and it, therefore, results in the increase of removal efficiency.

### 3.5. Effect of temperature

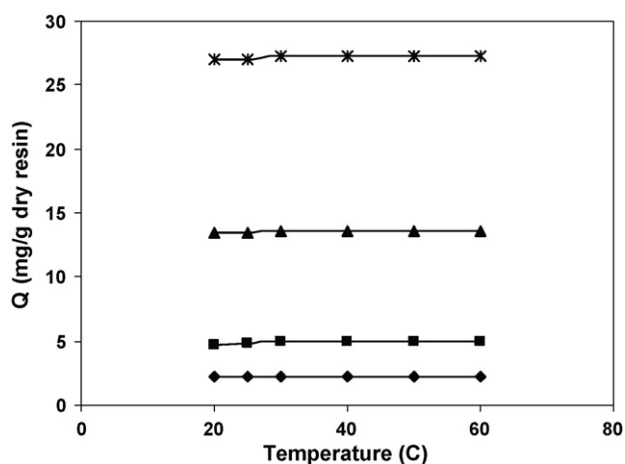
Temperature is a significant parameter controlling adsorption of species in a system. This is also a fact that most adsorption processes are exothermic in nature and hence lower temperatures favor the removal by the adsorption. In the present study, the removal of Cr(VI) in the temperature range of 20–60 °C for different concentrations of chromium solution was investigated (Fig. 8).

Table 2  
Values of Langmuir and Freundlich constants for the adsorption of Cr(VI).

T (K)	Langmuir constants				Freundlich constants		
	$R_L$	$Q^0$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L g}^{-1}$ )	$R^2$	$n$	$K_F$ ( $\text{L g}^{-1}$ )	$R^2$
293	0.003	74.62	14.28	0.9973	3.98	33.11	0.9998
303	0.008	82.46	16.56	0.9989	4.32	35.48	0.9998
313	0.011	94.34	18.33	0.9989	4.49	4.74	0.9950

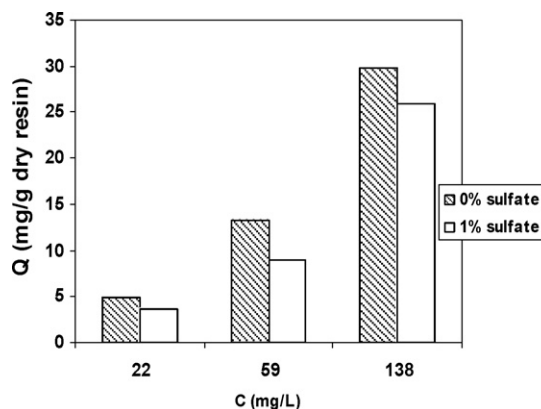


**Fig. 7.** Effect of the resin amount on the adsorption of Cr(VI) onto the PyR resin (concentration of the chromate solution,  $\blacklozenge$  13 mg L<sup>-1</sup>;  $\blacksquare$  22 mg L<sup>-1</sup>;  $\blacktriangle$  59 mg L<sup>-1</sup>); volume of the adsorption medium, 25 mL; temperature, 25 ± 1 °C; stirring time, 14 rpm; adsorption time, 24 h).



**Fig. 8.** Influence of temperature on the adsorption of Cr(VI) for PyR resin at different concentrations of the chromate solutions ( $\blacklozenge$  13 mg L<sup>-1</sup>;  $\blacksquare$  22 mg L<sup>-1</sup>;  $\blacktriangle$  59 mg L<sup>-1</sup>; \* 116 mg L<sup>-1</sup>) (volume of the adsorption medium, 25 mL; stirring time, 140 rpm; adsorption time, 24 h, temperature 25 ± 1 °C; amount of resin, 0.1 g).

This figure shows no effect of the temperature on the chromium adsorption capacity for the pyridine strong base anion exchanger. These results suggest that the adsorption of chromium ions takes place by the ionic mechanism and there is no possibility of the formation of some coordinate type of bond between chromium atom of chromate ion and electron rich donor atoms belonging to the



**Table 3**  
Thermodynamic parameters for the adsorption of Cr(VI) on pyridine resin.

T (K)	$\Delta G$ (KJ mol <sup>-1</sup> )	$\Delta H$ (KJ mol <sup>-1</sup> )	$\Delta S$ (KJ K <sup>-1</sup> mol <sup>-1</sup> )
293	-6.47	4.77	0.038
303	-6.88	4.77	0.038
313	-6.95	4.77	0.038

functional group attached to the quaternary nitrogen atoms.

Thermodynamic studies are used to explain any reaction in a better way. In this paper also, thermodynamic parameters namely,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined at 20, 30 and 40 °C. the values of these parameters have been given in Table 3.

The negative,  $\Delta G^\circ$  values indicate the process for pyridine resin to be spontaneous in nature of adsorption. Values of energy change decrease slightly by increasing the temperature. This revealed that the adsorption could be improved using higher temperature.

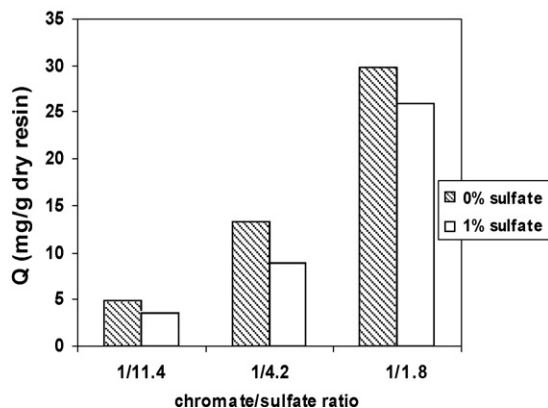
Positive values of entropy change and enthalpy change also indicate the endothermic nature of adsorption of Cr(VI) on pyridine strong base anion exchange resin.  $\Delta S^\circ$  can be used to describe the randomness at the resin-solution interface during the adsorption. Increase in the solution temperature has no effect on the adsorption. Therefore, a general temperature range is suggested to be 20–40 °C.

### 3.6. Effect of the $SO_4^{2-}$ ions

Addition of inorganic salts to the adsorption system is an effective way of influencing adsorption. Since sulfate and chloride are the predominant anionic species in cooling tower blow down, the resin must have high sorption preference for Cr(VI) over these competing anions for any possible application in chromate recovery process. The adsorption of Cr(VI) on the pyridine resin in chloride form in the binary system was studied using  $SO_4^{2-}$  anions as competitive counter ions. The results of these experiments are illustrated in Fig. 9.

As it can be seen the adsorption capacity of chromium was not influenced by the presence of sulfate ions even if they existed in the high amount in the solution.

It is well-known that the selectivity order for the common anions of the commercially styrene anion exchangers is the following  $SO_4^{2-} > I^- > CrO_4^{2-} > Br^- > Cl^-$ . In our case the synthesized resins have a reversal selectivity namely,  $CrO_4^{2-} > SO_4^{2-} > Cl^-$  for the concentration range of 22–119 mg L<sup>-1</sup>. The same behavior of pyridine strong base anion exchange resins in the competitive adsorption system of chromate/sulfate was observed in the previous studies [21].



**Fig. 9.** The effect of the sulfate anions on the adsorption capacity of PyR (volume of the adsorption medium, 25 mL; stirring time, 140 rpm; adsorption time, 24 h, temperature 25 ± 1 °C; amount of resin, 0.1 g; 1 wt.% Na<sub>2</sub>SO<sub>4</sub>).

The reason for the chromium selectivity over sulfate anion is due to the transition metal anion adsorption on the  $\pi$  bonds of the pyridine ring, formation a sandwich arrangement with the chromium anion and functional groups attached to the quaternary nitrogen atom.

#### 4. Conclusions

Nucleophilic substitution reaction of 4-VP:DVB copolymer with 2-chloroacetamide as halogenated compound led to the novel pyridine strong base anion exchange resin with amide functional groups attached to the quaternary nitrogen atoms. This resin of gel type structure exhibited good value of the strong base exchange capacity values.

Adsorption study of hexavalent chromium on new performed resin showed a good efficiency of the chromium ions. At high concentration of the chromate ions there are all types of chromium in the solution and functional groups attached to the matrices of the pyridine resins create an appropriate environment to ensure the ion exchange for a counter ion with no smaller equivalent volume and the high diameter of their hydrated forms. Pyridine resin has the higher than 90% degree of usage of the strong base exchange capacity which means a very good efficiency in the removal of Cr(VI).

The chromium concentration had a pronounced effect on the rate of adsorption, when the chromium concentration increased the adsorption rate also increased.

Temperature has a small effect on the Cr(VI) adsorption capacity essentially depending upon pH and concentration. The adsorption of chromium ions took place by the ionic mechanism with no possibility to form of some coordinate type of bond between chromium atom and electron donor atoms belonging to the functional groups attached to the quaternary nitrogen atom.

At low concentration of Cr(VI) the pyridine strong base anion exchanger offers much greater chromate removal capacity at acidic pH compared to alkaline pH. At the pH decrease, the ionic strength of the solution increases and as a consequence, the effectiveness of Cr(VI) adsorption onto pyridine resin with amide functional groups increases.

The experimental data well obeyed both Langmuir and Freundlich adsorption isotherms. Negative values of the  $\Delta G^\circ$  indicate the feasibility of adsorption of Cr(VI) on the yielded pyridine resin.

A comparison of Cr(VI) uptakes by different natural and synthetic adsorbents presented in the literature showed that the activated carbon and synthetic anion exchange resins based on styrene:divinylbenzene matrices have the highest removal capacities, i.e. 97.4% and 91.1%, respectively. The yielded pyridine strong base anion exchange resin are also able to remove Cr(VI) from aqueous solution more than 90% and moreover has the advantage to be selective towards these anions in the chromium/sulfate binary sorption experiment.

The pyridine resin exhibited the higher selectivity for Cr(VI) in the presence of sulfate anions as competitive counter ions than the commercial strong base anion exchange resins based on styrene:divinylbenzene copolymer. This selectivity is explained by

the adsorption of the transition metal anion on the  $\pi$  bonds of the pyridine ring and the formation a sandwich arrangement with chromium anion and amide functional groups attached to the quaternary nitrogen atoms.

Because the pyridine strong base anion exchange resins offer much higher resistance to oxidation than conventional strong base polystyrene anion exchange resins could be considered as a new alternative for the retention of chromate ions from the aqueous solutions.

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